Nanoscale Heat Transfer on the Picosecond Time scale

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ABSTRACT

Using the method of molecular dynamics, we have examined the decay of an instantaneously imposed heat pulse on an equilibrium model fluid similar to super-critical argon. The spatial extent of the initial pulse is quite small — on the order of 100 cubic nanometers; the amount of energy added to the system is only 5% of the total system kinetic energy. This small pulse decays quite rapidly, within several picoseconds, but the decay proceeds more slowly than predictions based on the hydrodynamic equations. During the first picosecond of the decay, the kinetic energy is not equipartitioned and a very fast process of energy transfer from kinetic energy to potential energy takes place. A good fit to the molecular dynamics data is obtained using a simple linear superposition of the hydrodynamic and free streaming theories.

I. Introduction

In this paper we examine the earliest stages of the time evolution of a heat pulse in a model fluid similar to super-critical argon. On the nanometer length scale and picosecond time scale we find, not surprisingly, significant deviations from hydrodynamic behavior.

Our purpose is to identify some of the non-hydrodynamic features of the heat-pulse

evolution on the picosecond time scale and their relation to hydrodynamics. Our study is

based on molecular dynamics calculations that indicate: (1) the relaxation of the heat pulse

is slower than that predicted by hydrodynamics; (2) during the first picosecond there is no

local equilibrium in the disturbed region; (3) at the very earliest times system behavior is

dominated by the simple 'free streaming' of particles; (4) there is no indication of

hyperbolic heat transfer; (5) the rapid decay of the temperature field is associated with an

exchange between the kinetic and potential energies of the system; and (6) a simple, ad hoc,

superposition of the free streaming and hydrodynamic theories describes the observed

density, velocity and temperature fields within their uncertainties.

In Section II we define how the heat pulse is initiated as well as the molecular

dynamics method used to calculate system properties as they evolve in space and time.

Hydrodynamic and free-streaming theories for this system are developed in Section III and

compared to the molecular dynamics results. In Section IV we explain an ad hoc approach

that adequately describes the system's behavior.

II. Molecular Dynamics

The Verlet algorithm [1] is used to generate the phase space trajectories of $N =$

18000 particles in a rectangular volume, V, with periodic boundary conditions. The

spherically-symmetric, pairwise-additive, inter-particle force is determined by the Lennard-

Jones/spline potential [2]: $\boldsymbol{j}(r) = 4\boldsymbol{e}[(\boldsymbol{s}/r)^{12} - (\boldsymbol{s}/r)^6]$, $0 < r < r_c$; $= a(r - r_s)^2 +$

$b(r - r_s)^3$, $r_c < r < r_s$; $= 0$, $r_s < r$, where r is the distance between two particles,

$a = -(24192/3211)(\boldsymbol{e}/r_c^2)$, $b = -(387072/61009)(\boldsymbol{e}/r_c^3)$, $r_c = (26/7)^{1/6}\boldsymbol{s}$, and

$r_s = (67/48)r_c$. This potential is a finite-ranged modification of the well known Lennard-Jones 12-6 potential of depth e and diameter s, designed specifically to avoid the numerical problems associated with the truncation of the infinite-ranged Lennard-Jones potential, viz. discontinuities in the interparticle force. r_c is the point of inflection of the attractive tail of the Lennard-Jones potential. r_s, a, and b are determined by requiring the Lennard-Jones/spline potential and its first two derivatives to be continuous at r_c.

The particle mass, m, the Boltzmann constant k_B, and the Lennard-Jones parameters, e and s, allow the definition of a set of dimensionless variables (denoted by a superscript *) that are used to generate the molecular dynamics trajectories and define other derived quantities. The time unit is $s(m/e)^{1/2}$, the length unit is s, the velocity unit is $(e/m)^{1/2}$, the energy unit is e, and the temperature unit is e/k_B. If we set $e/k_B = 119.8 \ K$, $s = 3.405 \times 10^{-10} meters$, and $m = 39.94 \ kg/kmol$, values appropriate for Ar, then $t^* = 1$ corresponds to 2.16 ps, $x^* = 1$ to 0.3405 nm, $v^* = 1$ to 568 km/h, $n^* = 0.5$ to 21.03 kmol/m^3, and $T^* = 2$ to 239.6 K.

II.1 The initial phase points

The ensemble of initial phase points of the system are constructed in two steps. First a system phase point is sampled from an equilibrium molecular dynamics ensemble (N, V, E, and $P = 0$, fixed, where E is the total energy and P the total momentum). The average T^* of the ensemble is 2.0. Then, the initial 'heat' or 'temperature' pulse is created by multiplying the velocity of every particle with x-coordinates in the interval ($0.45L_x$,

$0.55L_x$) by $(3/2)^{1/2}$, where $V = L_x L_y L_z$. Since the particles in this region have a velocity distribution that is essentially [3] Maxwellian, this rescaling does not change the form of the velocity distribution but it does change its dimensionless 'temperature' from 2.0 to 3.0 in the region of the pulse. The total energy of the system has increased to E', but the potential energy remains constant.

The initial states formed in this manner are not equilibrium states, although they have some features of equilibrium states: (1) the spatial configuration of particles has all the characteristics of an equilibrium state with $T^* = 2$; (2) the two local velocity distributions are (essentially) Maxwellian; and (3) the local kinetic energy is equipartioned. However, the local kinetic energy is not uniform in the x-direction and the average total kinetic energy deviates significantly from its equilibrium value for a system with total energy E'.

II.2 Relaxation to equilibrium

In order to quantify how this system evolves in time, we use the method of molecular dynamics to generate the phase-space trajectories. A time step of $\Delta t^* = 0.002$, is used to advance an initial phase point forward in time. At selected time intervals various physical properties, e.g., the local number density, are calculated. The average of these properties over a sample of N_E members of the initial ensemble is then determined.

The spatial variations of system properties are determined by dividing the volume into 100 thin slabs of size $L_x / 100 \times L_y \times L_z$. In all of the calculations reported here $N = 18000$ and n^* is either 0.5 or 0.2, so that $L_x/\sigma = 10$ or 13.572, respectively. L_y and L_z were

chosen much larger than L_x ($L_y=L_z=6L_x$) so that layers perpendicular to the x-axis as thin as

$L_x/100$ contain substantial numbers of particles.   The lth slab is centered about

$x_l = (l-1/2)L_x/100$. A physical property $Q(x_l,t)$ of the system is calculated by

$$Q(x_l,t) = \frac{1}{N_E}\sum_{j=1}^{N_E} Q_l^j(t) \quad ,$$

where $Q_l^j(t)$ is the value of Q in layer l at time t for the jth member of the initial ensemble.

For instance, the x-component of the local velocity $v_x(x_l,t)$ is given by

$$v_x(x_l,t) = \frac{1}{N_E}\sum_{j=1}^{N_E} v_x^j(x_l,t), \quad v_x^j(x_l,t) = \frac{\sum_{i=1}^{N} c_l[r_{xi}^j(t)]v_{xi}^j(t)}{\sum_{i=1}^{N} c_l[r_{xi}^j(t)]} \quad ,$$

where $c_l[r_{xi}^j]$ is the characteristic function for layer l. We define the local temperature in

terms of the kinetic energy in the local center of mass frame. In our system we define

component temperatures by

$$T_a(x_l,t) = \frac{1}{N_E}\sum_{j=1}^{N_E} \frac{m\sum_{i=1}^{N} c_l[r_{xi}^j(t)](v_{xi}^j(t)-v_a^j(x_l,t))^2}{\sum_{i=1}^{N} c_l[r_{xi}^j(t)]} \quad ,$$

where $a = x, y, or\ z$. The (average total) temperature $T(x_l,t)$ is given by

$T(x_l,t) = \frac{1}{3}\left(T_x(x_l,t)+T_y(x_l,t)+T_z(x_l,t)\right)$. When local equilibrium is established T is
equivalent to the local thermodynamic temperature.

    The ensemble averaged dynamics, and consequently also the properties of this

system, are calculated over time intervals short enough so that the initial disturbance of the

heat pulse does not reach either the $x = 0$ or $x = L_x$ boundary. For the case $n^* = 0.5$ this time interval is $t^* = 0.4$; for $n^* = 0.2$ it is $t^* = 0.6$; and in both cases $N_E = 60$. As shown in Figs. 1 and 2, the expansion of the initial pulse generates changes in the density and velocity fields. These disturbances propagate at roughly the (equilibrium) sound speed. $T(x,t)$ and $(T_z + T_y)/T_x$ are shown in Figs. 3 and 4, respectively. The spreading of the initial temperature field in the x-direction matches the disturbances in the density and velocity fields. The initial temperature field decays in magnitude very rapidly. During the time intervals examined local equilibrium is never obtained in the disturbed regions since $(T_z + T_y)/T_x$ is significantly different from the equipartition value of 2. Although $T(x,t)$ remains symmetric and unimodal, as a function of x, the x-dependence of T_x is significantly different from that of T_y and T_z, which leads to the appearance of a small 'shoulder in $T(x,t)$. The lack of equipartition and the 'shoulders' observed in $T(x,t)$ appear to be connected to the formation of the sound wave. We did not observe any qualitative differences between the $n^* = 0.2$ and $n^* = 0.5$ cases, except that the pulse spreads more slowly at the lower density. [A single error bar is shown in each figure to give a general impression of the statistical certainty of the results.]

III. Theory

We find, as explained below, that even though local equilibrium is not established, the hydrodynamic solution captures many of the qualitative features of the time evolution of the pulse. However, hydrodynamics predicts a faster spreading of the initial pulse than observed, perhaps indicating that hydrodynamic heat conduction (in local equilibrium)

provides an optimal mode of energy transfer and for very short times that 'ordered' mode is not sufficiently established.

At very short times the particle motion is not affected by the interparticle interactions because the average force on particles is zero in the initial state. The 'free-streaming' behavior of the system, including T_x, T_y, and T_z, can then be explicitly evaluated. Although the free streaming theory (FS) is quantitatively correct only for very short times, it provides a remarkably good qualitatively description of the density and velocity fields over the entire duration of the simulations. However, since it ignores interparticle interactions it does not account for the relaxation of the potential energy of the system and the decay of $T^{FS}(x,t)$ is much slower than observed.

As we show below, the observed behavior lies between the predictions of these two theories.

III.1 Hydrodynamics

The initial state is symmetric and uniform in the y- and z-directions so the complete set of hydrodynamic equations describing the density, velocity, and temperature fields are one dimensional. The initial conditions are: $n(x,0)\boldsymbol{s}^3/m = 0.5 \, or \, 0.2, \quad v_x(x,0) = 0$, and $k_BT/\boldsymbol{e} = 3.0$ for x in $[0.45L_x, 0.55L_x]$ and $k_BT/\boldsymbol{e} = 2.0$ elsewhere. The boundary conditions are periodic.

A numerical solution of these equations is obtained using a standard forward-time, space-centered algorithm [4]. We have assumed that the specific heat at constant volume, the shear viscosity, the bulk viscosity, and the thermal conductivity are constant and have

obtained their values from independent molecular dynamics calculations at the initial density and $T^* = 2;$ we used an equilibrium equation of state for the Lennard-Jones/spline system.

Given that local equilibrium, in particular the equipartition of kinetic energy, has not been established, it is remarkable that the hydrodynamic description, n^H, v_x^H, T^H, shown in Figs. 1, 2, and 3, is not too far off. The hydrodynamic solution decays and spreads too fast, however. The temperature field does not develop the shoulders observed in $T(x,t)$ and the velocity field appears to be qualitatively different than v_x in the center of the system.

III.2 Free streaming

If we make a Taylor series expansion of the position and velocity variables about $t = 0$, then the position and velocity of particle i at time t can be expressed in terms of the initial positions and velocities, $\vec{r}_i(0)$ *and* $\vec{v}_i(0)$, as well as other force related quantities that characterize the initial state. The most elementary, short-time, approximation to these expansions is the free-streaming (no forces) approximation (FS): $\vec{r}_i^{FS}(t) = \vec{r}_i(0) + \vec{v}_i(0)t$; $\vec{v}_i^{FS}(t) = \vec{v}_i(0)$. The time interval over which this approximation is accurate depends on the influence of the interparticle forces, but even in dense fluids there is a time interval small enough such that free streaming equations are a good approximation. For the initial states considered here, $\vec{r}_i^{FS}(t)$ *and* $\vec{v}_i^{FS}(t)$ are not accurate approximations (for arbitrary i) for more than a few molecular dynamics time steps, roughly 0.01 in reduced time units. However, we find that ensemble averaged physical properties are accurate over a somewhat

longer time interval and over the time interval of the molecular dynamics simulations they display most of the qualitative features seen in the molecular dynamics calculations.

Since the initial states we consider have a uniform density and the velocity distributions are Maxwellian, the ensemble-averaged density, velocity, and kinetic energy fields are given by

$$n^{FS}(\vec{r},t) = \int d\vec{w}\, n(\vec{r} - \vec{w}t,0) f(\vec{w};\vec{r} - \vec{w}t,0) \quad,$$

$$n^{FS}(\vec{r},t) v^{FS}(\vec{r},t) = \int d\vec{w}\, \vec{w} n(\vec{r} - \vec{w}t,0) f(\vec{w};\vec{r} - \vec{w}t,0) \quad,$$

$$n^{FS}(\vec{r},t) k_B T_a^{FS}(\vec{r},t) = \frac{m}{3}\int d\vec{w}(\vec{w} - \vec{v}^{FS})^2 n(\vec{r} - \vec{w}t,0) f(\vec{w};\vec{r} - \vec{w}t,0) \ ,$$

where $f(\vec{w};\vec{r} - \vec{w}t,0)$ is the Maxwell velocity distribution at position $\vec{r} - \vec{w}t$ at $t = 0$.

The FS density and velocity fields, as well as $(T_y^{FS} + T_z^{FS})/T_x^{FS}$, are shown in Figs. 1, 2 and 4 respectively. For $n^* = 0.5$ the FS approximations match the MD results for times $t^* \le 0.15$; for $t^* > 0.15$ the FS approximations deviate significantly from the MD results, but still match the general qualitative spatial variations. $T^{FS}(x,t)$ is shown in Fig. 3. For $n^* = 0.5$ and $t^* < 0.05$ and for $n^* = 0.2$ and $t^* < 0.1$ $T^{FS}(x,t)$ gives a good description of the temperature field; beyond these time there are significant deviations from $T(x,t)$. We note, however, that $T^{FS}(x,t)$ does exhibit the 'shouldered pulse' feature seen in the MD results.

In the FS approximation the temperature pulse does not decay in magnitude as rapidly or spread out spatially as fast as $T(x,t)$. Since the FS kinetic energy is conserved there is no mechanism for the transfer of energy to the potential energy field. This appears

to be the reason that the FS pulse magnitude remains much larger than the MD results. The effects of this kinetic/potential relaxation can be easily incorporated into the FS equations by replacing the temperature $T(\vec{r} - \vec{w}t, 0)$ in $f(\vec{w}; \vec{r} - \vec{w}t, 0)$ by a time-dependent effective temperature. This effective temperature can be determined from a molecular dynamics study of kinetic/potential relaxation [5].

IV. An Ad Hoc Approach

The initial stage of the heat-pulse decay is, in many respects, dominated by the simple 'free-streaming' motion of the particles — not by hydrodynamics. At later times, but before true local equilibrium has been established, the decay appears to be described well by hydrodynamics. We have not yet developed a consistent theory that spans these two stages. However, we find that a simple ad hoc method that can be used until a comprehensive theory is developed.

The ad hoc method is simply a linear superposition of the hydrodynamic and FS theories (the LS approach). For a given density, the linear superposition approach is defined by

$$Q^{LS}(x,t) = \boldsymbol{g}(t)Q^{FS}(x,t) + (1 - \boldsymbol{g}(t))Q^{H}(x,t) \quad ,$$

where the superscript LS denotes the linear superposition quantity and Q is either n, v_x, or T. The time-dependent parameter $\boldsymbol{g}$ should approach 1 as t approaches 0 and should approach 0 as t becomes 'large'. For a given t and Q, $\boldsymbol{g}$ can be determined empirically by the method of least squares. We find that at fixed t, $\boldsymbol{g}$ is nearly the same for all choices of Q, and for a given Q, $\boldsymbol{g}$ decreases exponentially with time. Thus, we set $\boldsymbol{g}(t) = \exp[-t/\boldsymbol{t}]$,

where $\boldsymbol{t}$ is independent of t and Q. Then $\boldsymbol{t}$ becomes a time that characterizes the duration of the free-streaming dominance.

In the case of self diffusion, free streaming dominates at times for which

$D(t) \rightarrow k_B Tt/m \ \ (as \ t \rightarrow 0)$, where $D(t) = \int_0^t ds < v_{xi}(0)v_{xi}(s)>$. This suggests

$\boldsymbol{t} < D(\infty)/[k_B T/m]$. Using the self-diffusion coefficient data of Kincaid et al. [6] we find

that setting $\boldsymbol{t} = \dfrac{4}{5}D(\infty)/[k_B T/m]$ allows the LS approach to fit the simulation data to

within its statistical uncertainty as shown in Figs. 1, 2, and 3. The density dependence of

$D(\yen)$ matches the density dependence of $\boldsymbol{t}$. [$\boldsymbol{t}^* = 0.52$ for $n^* = 0.2$ and $\boldsymbol{t}^* = 0.16$ for $n^* = 0.5$.]

V. Final Remarks

The initial stage of the time evolution of the heat pulse considered here is distinctly non-hydrodynamic. For the systems studied, the duration of this stage is on the order of a picosecond. For heat pulses of macroscopic size the deviations from hydrodynamic behavior will be negligible. On the nanometer scale, however, significant heat transfer takes place but at a rate slower than hydrodynamics. This phenomenon may be important in processes such as pulsed laser annealing of silicon [7] and the development of nano devices.

It has been suggested by many authors [8] that heat conduction should be described by hyperbolic equations -- essentially a damped wave equation. Here, as for the case of self diffusion [9], we have not observed any evidence of a propagating temperature wave.

LIST OF SYMBOLS

N   number of particles

V   volume

E, E'   total energy

P   total momentum

r   position

t, Δt time

m   particle mass

n   N/V

v   velocity

T, T_x, T_y, T_z temperature

Q   system property

D   self-diffusion coefficient

N_E number of ensemble samples

k_B Boltzmann's constant

$\vec{w}$ velocity

f   Maxwell velocity distribution

$\boldsymbol{j}$ interparticle potential

$\boldsymbol{e}, \boldsymbol{s}, a, b$ interparticle potential parameters

$\boldsymbol{c}$ characteristic function

γ linear superposition parameter

t characteristic time

superscripts

   *   dimensionless variable

   FS   free streaming approximation

   H   hydrodynamics

   LS   linear superposition approximation

subscripts

   i   particle-number index

   j   ensemble-member index

   l layer number

REFERENCES

1. L. Verlet, Phys. Rev. 159 (1967) 98-103.

2. B. L. Holian, D. J. Evans, J. Chem. Phys 78 (1983) 5147-5150.

3. J. R. Ray, H. W. Graben, Phys. Rev. A 44 (1991) 6905-6908.

4. W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling, Numerical Recipes (Cambridge Univ. Press, 1986, Cambridge) 615-641.

5. J. M. Kincaid, E. G. D. Cohen, E. Hernandez, in preparation (2000).

6. J. M. Kincaid, R.-F. Tuo, M. Lopez de Haro, Mol Phys. 81 (1994) 837-850.

7. A. Majumdar in *Microscale Energy Transport*, C.-L. Tien, A. Majumdar, F. M. Gerner (Taylor & Francis, 1998, Washington, D.C.) 3-93.

8. See for instance, D. D. Joseph, L. Preziosi, Rev. Mod. Phys. 61 (1989) 41-75; 622

(1990) 375-393.

9. J. M. Kincaid, Phys. Rev. Lett. 74 (1995) 2985-2988.

FIGURE CAPTIONS

Fig. 1 The density, $n^*(x,t)$, as a function of position, x^*, for the case $n^* = 0.5$ and $t^* = 0.2$.

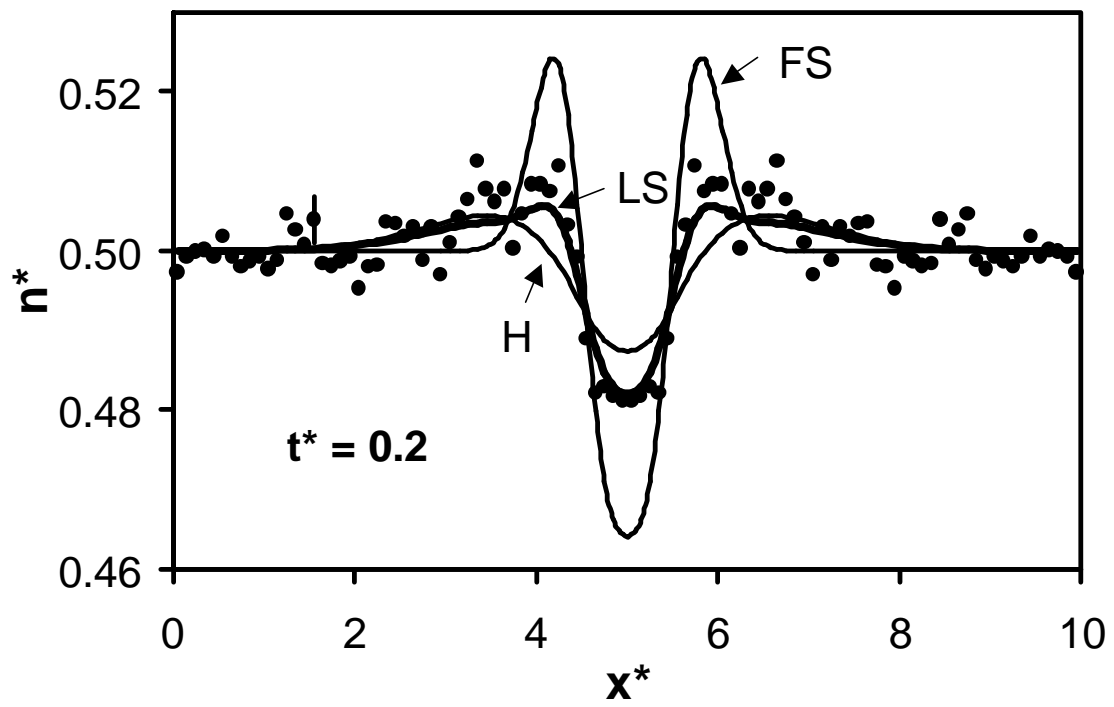[molecular dynamics •, hydrodynamics H, free streaming FS, linear superposition LS]

Fig. 2 The local fluid velocity in the x-direction, $v_x^*(x,t)$, as a function of position, x^*, for

the case $n^* = 0.5$ and $t^* = 0.2$. [molecular dynamics •, hydrodynamics H, free streaming

FS, linear superposition LS]

Fig. 3 The temperature, $T^*(x,t)$, as a function of position, x^*, for the case $n^* = 0.5$ and $t^* =$

0.2. [molecular dynamics •, hydrodynamics H, free streaming FS, linear superposition LS]

Fig. 4 The component temperature ratio, $(T_y+T_z)/T_x$ as a function of position, x^*, for the

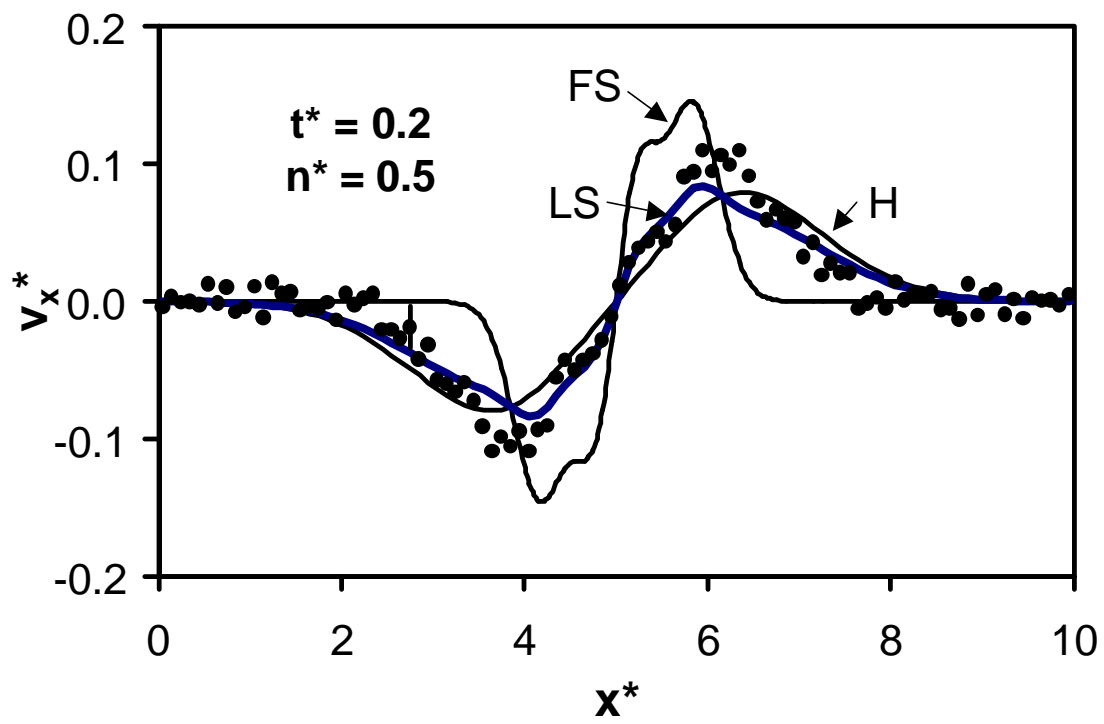case $n^* = 0.5$ and $t^* = 0.1$. In equilibrium systems the ratio is equal to 2.[molecular

dynamics •, free streaming FS]
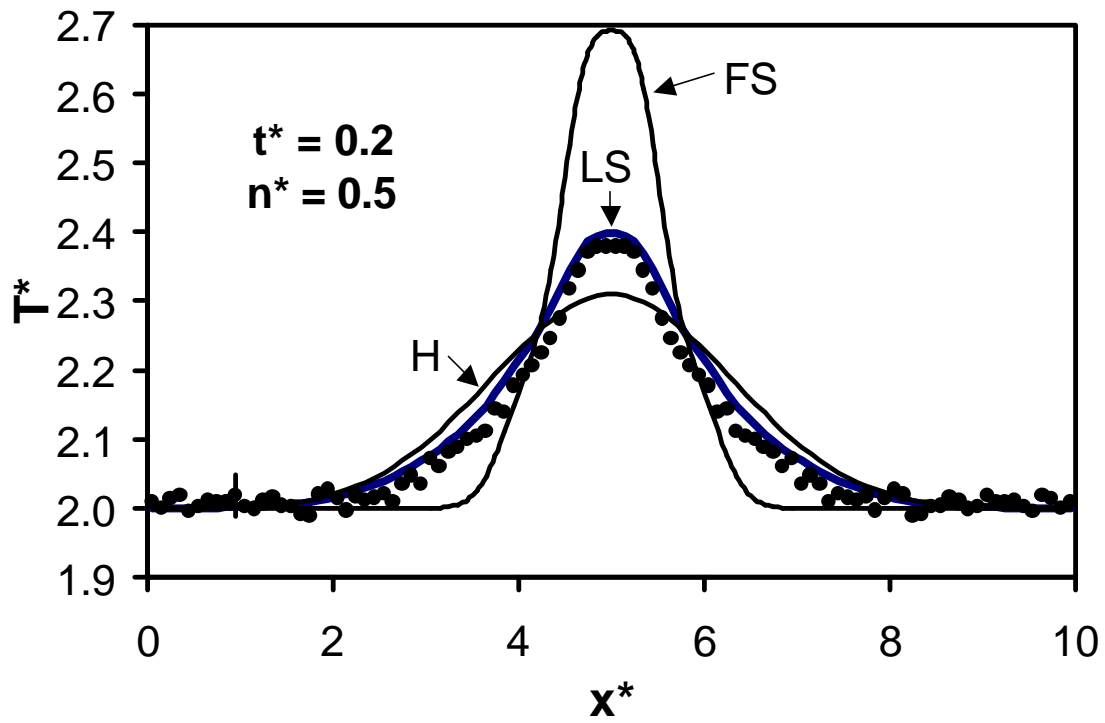
FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4